Supplementary information for

A simple approach for the discrimination of surfactants based on the control of squaraines aggregation

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Experimental Section

Materials

Sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), dodecyl sodium carbonate (SDC), sodium monododecyl phosphate (SDP), hexadecyl trimethyl ammonium bromide (CTAB), Triton X-100 reagents were purchased from Aladdin (China). Other chemicals and solvents were used as received if not noted. Probe squaraine (**SQ**) dye, was synthesized and purified as reported previously. [S1]

Measurements

Fluorescence and absorption spectra were collected by using a RF-5301 fluorescence spectrometer (Japan) and a Shimadzu 1750 UV-visible spectrometer, respectively. X-ray power diffraction (XRD) spectra were obtained by using Rigaku miniflex 600.

Sample Preparation, Data Acquisition and Analysis

All measurements were performed at 25 ^{0}C. Stock solution of **SQ** (5.0×10^{-4} M) was prepared in ethanol and diluted in distilled water (pH 7.0) to 5.0×10^{-6} M for titration experiments. Stock solutions of Sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), dodecyl sodium carbonate (SDC), sodium monododecyl phosphate (SDP), hexadecyl trimethyl ammonium bromide (CTAB), Triton X-100 were prepared in distilled water and diluted in distilled water (pH 7.0) for titration

experiments. UV and emission spectra were monitored within 20 seconds. There were three measurements at each concentration for one sample. Urine was collected from different adult volunteers and filtrated with 0.4 μM filter membrane. The filtrates were diluted 5 times with distilled water for use.

All data for LDA were collected from absorption spectra of **SQ**/surfactants. In water solution, each of surfactant was selected three different concentrations including 3.33 μM, 33.33 μM and 400 μM. The absorbance at 470, 488, 518, 528, 548, 568, 588, 598, 624 and 700nm were submitted to perform variable as the following formula: variable 1= $(A_{470}\text{-}A_{700})$ / A_{568}, variable 2= $(A_{488}\text{-}A_{700})$ / A_{568}, variable 3= $(A_{518}\text{-}A_{700})$ / A_{568}, variable 4= $(A_{528}\text{-}A_{700})$ / A_{568}, variable 5= $(A_{548}\text{-}A_{700})$ / A_{568}, variable 6= $(A_{588}\text{-}A_{700})$ / A_{568}, variable 7= $(A_{598}\text{-}A_{700})$ / A_{568}, variable 8= $(A_{624}\text{-}A_{700})$ / $A568$. In urine sample, each of surfactant was selected three different concentrations including 53.33，234.00，400.00 μM. The absorbance at 446, 466, 470, 486, 522nm，567nm，590nm，626nm，645nm，700 nm were submitted to perform variable as the following formula:

VAR1=（A_{446}-A_{700}）/A_{522}，
VAR2=（A_{466}-A_{700}）/A_{522}，
VAR3=（A_{470}-A_{700}）/A_{522}，
VAR4=（A_{486}-A_{700}）/A_{522}，
VAR5=（A_{567}-A_{700}）/A_{522}，
VAR6=（A_{590}-A_{700}）/A_{522}，
VAR7=（A_{626}-A_{700}）/A_{522}，
VAR8=（A_{645}-A_{700}）/A_{522}，

The input is:

```
USE HAO1
LABEL SPECIES / 1="SDS", 2="SDBS", 3="SDC", 4="SDP", 5="CTAB", 6="Triton X-100"
DISCRIM
    MODEL SPECIES = VAR1..VAR8
    PLENGTH / MEANS CLASS JCLASS
    ESTIMATE
```

In the process of data analysis, LDA was used and Jackknifed classification matrices were taken to evaluate discrimination results. The main results are listed as follow:

Table. S1 All average values of eight variables for six surfactants in water.

variable	SDS	SDBS	SDC	SDP	CTAB	Triton X-100
1	4.114	2.027	0.06	0.384	-0.005	-0.004
2	1.171	1.355	0.167	0.6	0.038	0.058
3	0.503	0.736	0.636	0.61	0.398	0.38
4	1.321	1.142	1.1	1.135	1.045	0.795
5	0.711	0.786	0.84	0.806	0.784	0.744
6	1.135	0.882	0.647	0.641	0.445	0.514
7	1.026	0.74	0.6	0.565	0.374	0.454
8	1.437	0.648	0.763	0.623	0.57	0.699

Table. S2 Summary of the Jackknifed Classification Matrix for six surfactants in water.

	SDS	SDBS	SDC	SDP	CTAB	Triton X-100	correct%
SDS	9	0	0	0	0	0	100
SDBS	0	9	0	0	0	0	100
SDC	0	0	9	0	0	0	100
SDP	0	0	0	9	0	0	100
CTAB	0	0	0	0	9	0	100
Triton X-100	0	0	0	0	0	9	100
Total	9	9	9	9	9	9	100

Table. S3 Group Frequencies

SDS	SDBS	SDC	SDP	CTAB	Triton X-100
9	9	9	9	9	9

Table. S4 All average values of eight variables for six surfactants in urine.

	SDS	SDBS	SDC	SDP	CTAB	Triton X-100
VAR1	-0.493	0.016	0.312	0.325	0.462	-0.049
VAR2	2.536	2.050	0.386	0.408	0.497	0.114
VAR3	3.340	2.633	0.404	0.458	0.505	0.142
VAR4	2.391	2.341	0.426	0.456	0.493	0.193
VAR5	0.317	0.749	0.971	0.916	0.906	0.965
VAR6	2.049	0.429	0.229	0.303	0.875	0.177
VAR7	3.574	0.347	0.149	0.187	1.220	0.212
VAR8	5.953	0.678	0.108	0.167	0.630	0.235

Table. S5 Summary of the Jackknifed Classification Matrix for six surfactants in urine.

	SDS	SDBS	SDC	SDP	CTAB	Triton X-100	correct%
SDS	9	0	0	0	0	0	100
SDBS	0	9	0	0	0	0	100
SDC	0	0	9	0	0	0	100
SDP	0	0	0	9	0	0	100
CTAB	0	0	0	0	9	0	100
Triton X-100	0	0	0	0	0	9	100
Total	9	9	9	9	9	9	100

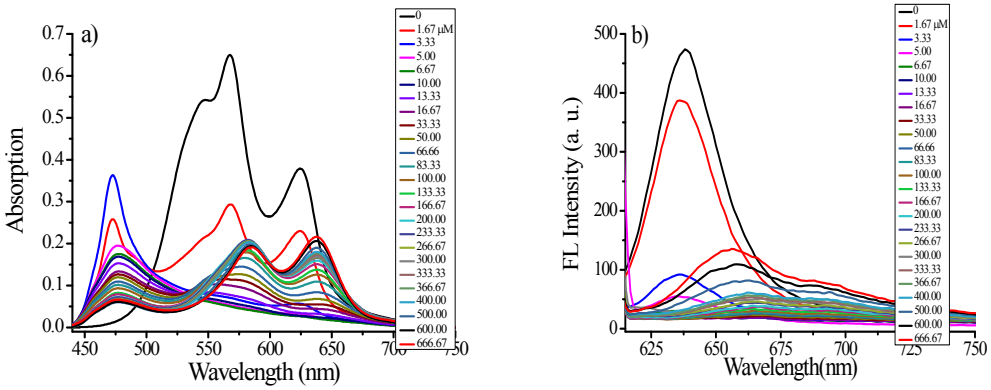


Fig. S1 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDBS in distilled water (pH 7.0). (λ_{ex} = 600 nm)

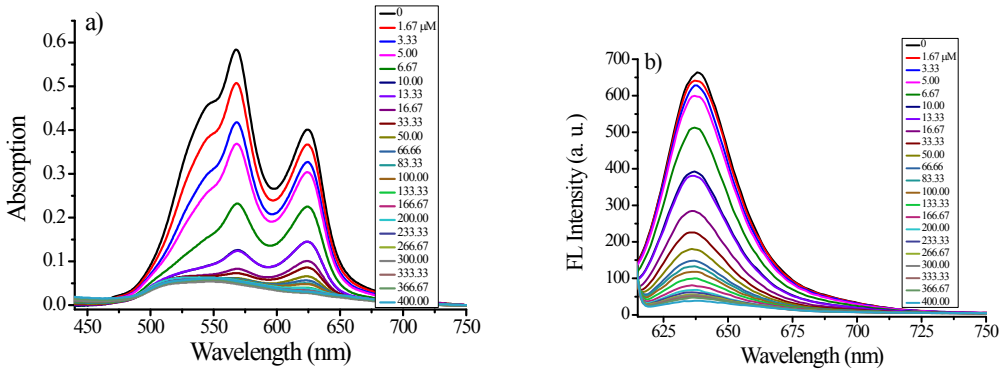


Fig. S2 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDC in distilled water (pH 7.0). (λ_{ex} = 600 nm)

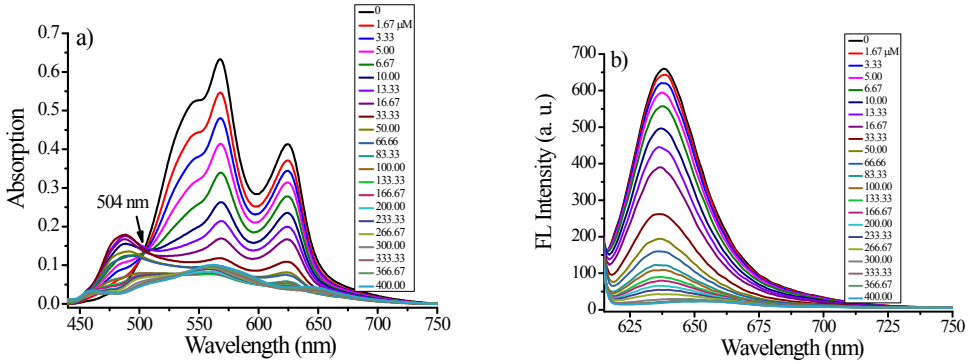


Fig. S3 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDP in distilled water (pH 7.0). (λ_{ex} = 600 nm)

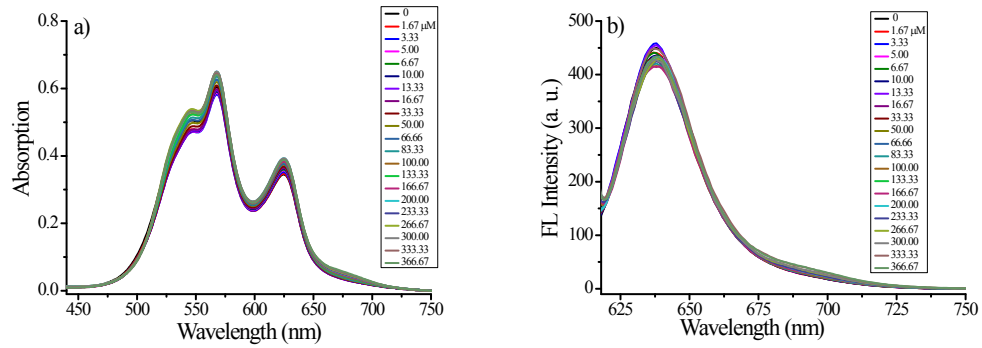


Fig. S4 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of CTAB in distilled water (pH 7.0). (λ_{ex} = 600 nm)

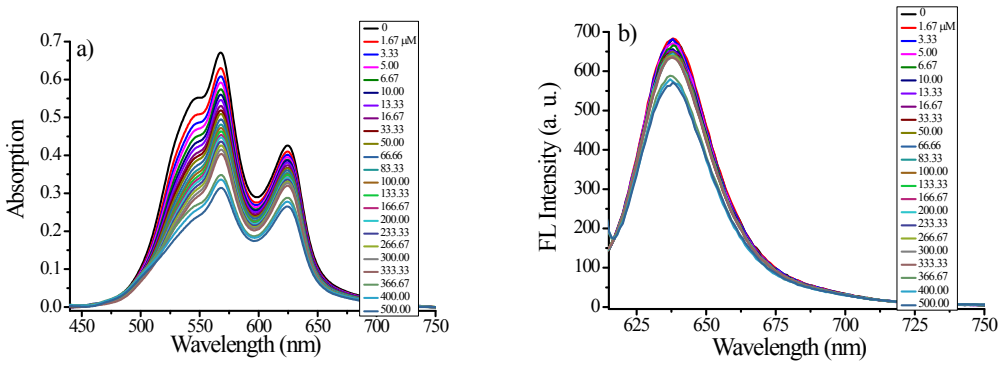


Fig. S5 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of TritonX-100 in distilled water (pH 7.0). (λ_{ex} = 600 nm)

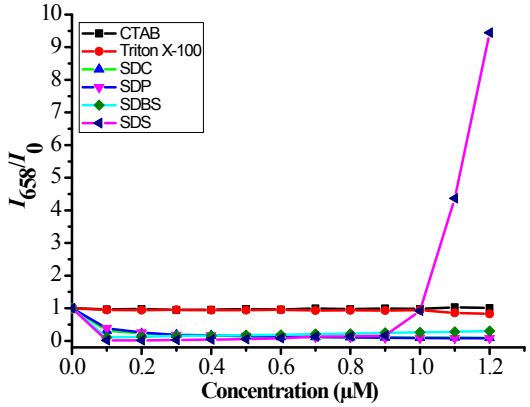


Fig. S6 Plots of relative fluorescent intensity changes (I_{658}/I_0) of probe **SQ** (5 μM) in distilled water (pH 7.0) induced by the addition of different amounts of surfactants as indicated. I_0 indicates the fluorescence intensity of free surfactants, while I_{658} indicated the fluorescence intensity upon addition of surfactants.

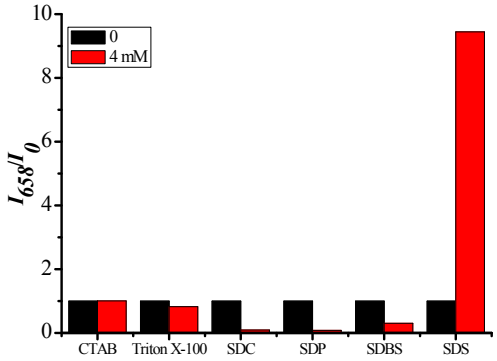


Fig. S7 Plots of relative fluorescent intensity changes (I_{658}/I_0) of probe **SQ** (5 μM) in distilled water (pH 7.0) induced by the addition of different amounts of surfactants as indicated. Black bars indicate the fluorescence intensity of free surfactants, while red bars indicated the fluorescence intensity upon addition of surfactants [surfactants] = 0.4 mM.

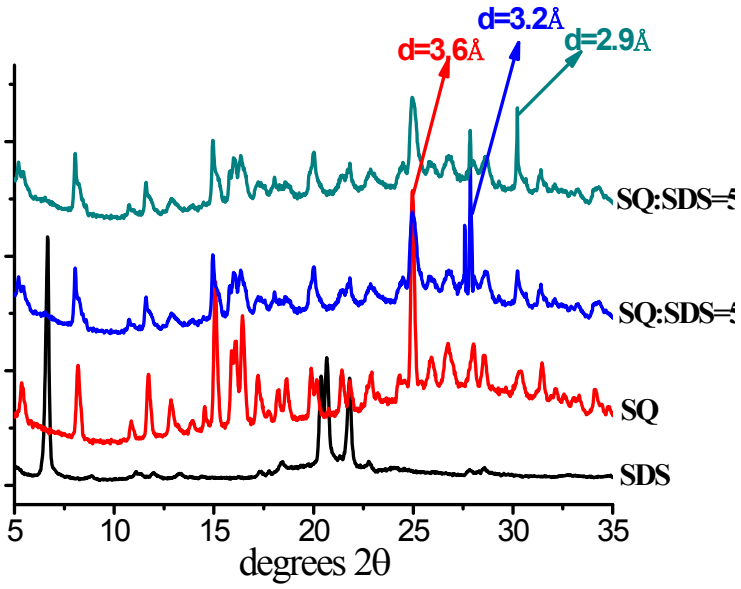
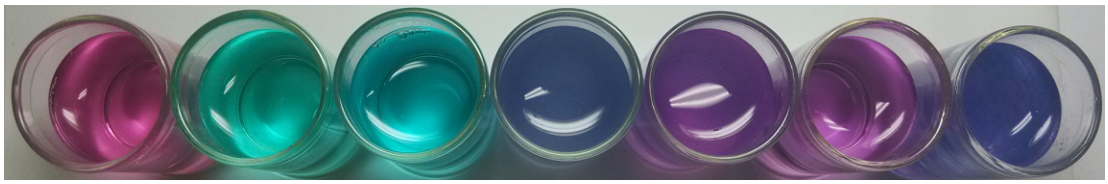


Fig. S8 X-ray powder diffraction patterns of **SQ** in the absence and presence of SDS.



Blank SDS SDBS SDP SDC Triton X-100 CTAB

Fig. S9 Colorimetric responses of probe **SQ** (0.075 μM) in urine induced by the addition of various surfactants (3.00 μM) as indicated.

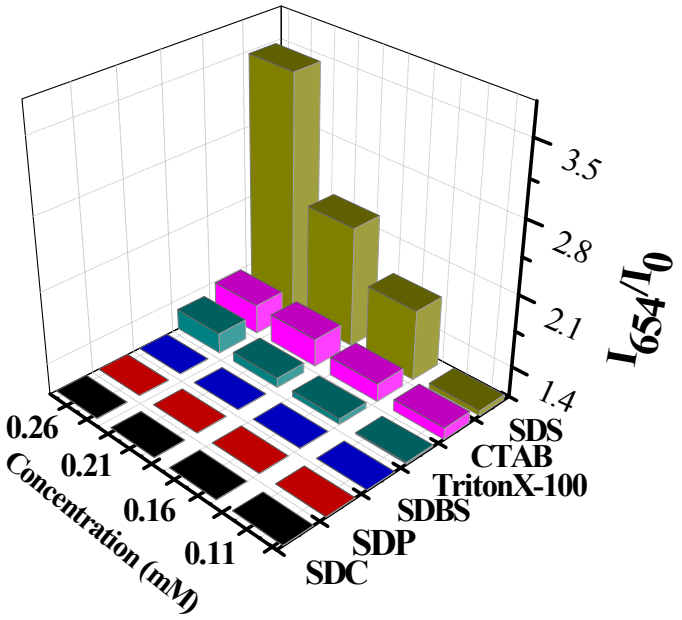


Fig. S10 Plots of relative fluorescent intensity changes (I_{658}/I_0) of probe **SQ** (5 μM) in urine induced by the addition of different amounts of surfactants as indicated. I_0 indicates the fluorescence intensity of free surfactants, while I_{658} indicated the fluorescence intensity upon addition of surfactants.

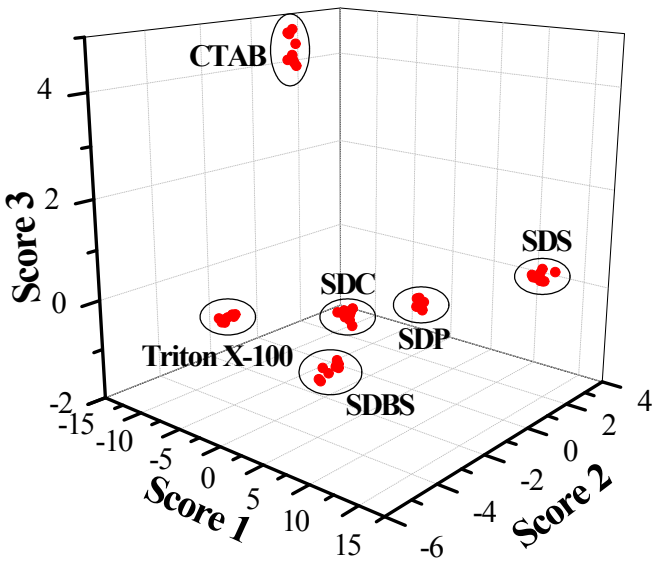


Fig. S11 Three-dimensional LDA score plot of probe **SQ** (5 μM) in urine induced by the addition of surfactants (3.00 μM) as indicated.

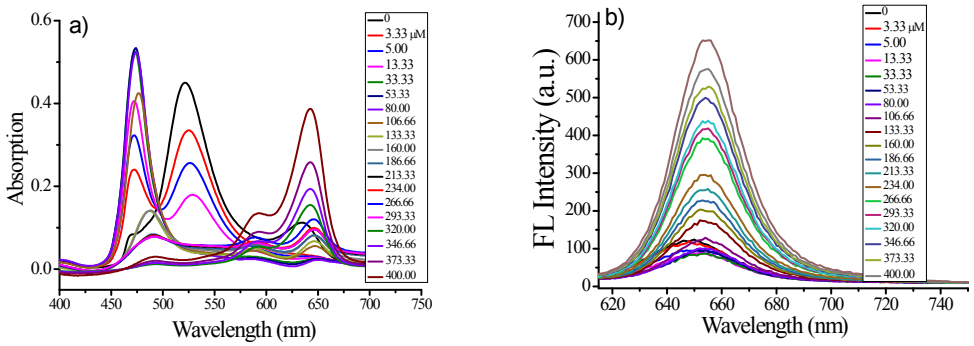


Fig.S12 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDS in urine. (λ_{ex} = 600 nm)

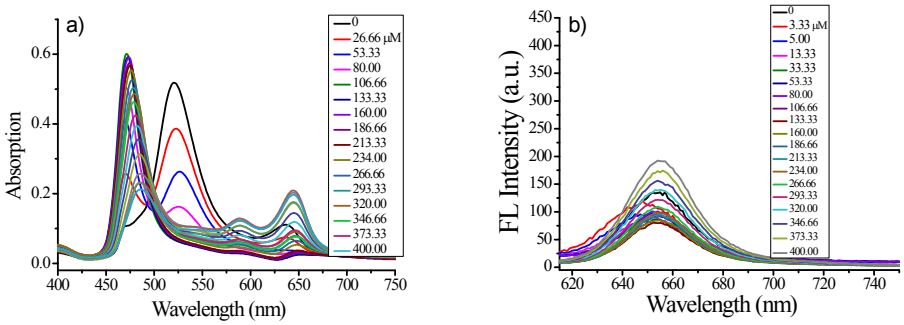


Fig.S13 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDBS in urine. (λ_{ex} = 600 nm)

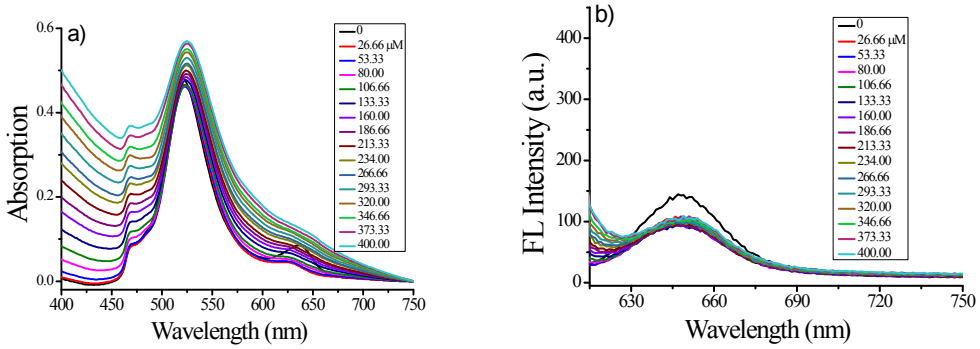


Fig.S14 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDC in urine. (λ_{ex} = 600 nm)

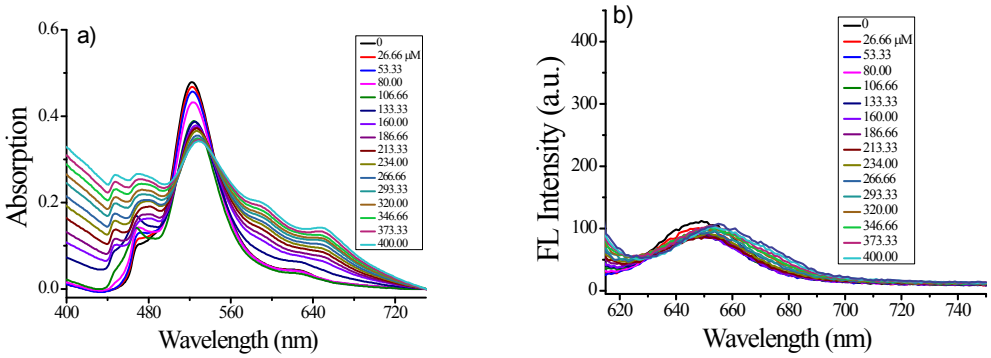


Fig.S15 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of SDP in urine. (λ_{ex} = 600 nm)

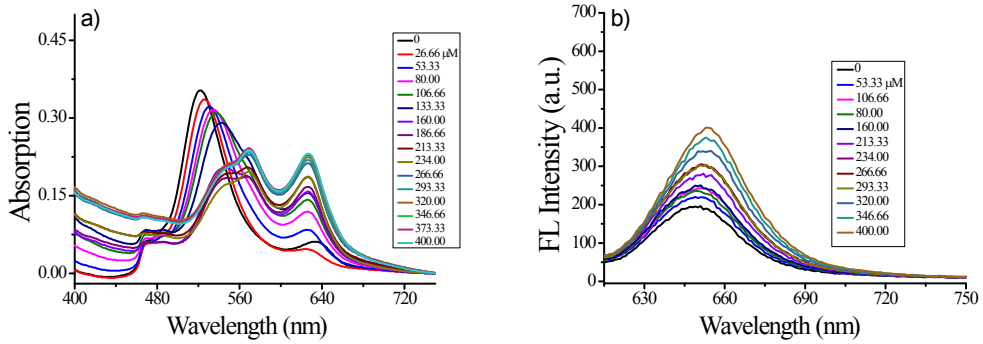


Fig.S16 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of CTAB in urine. (λ_{ex} = 600 nm)

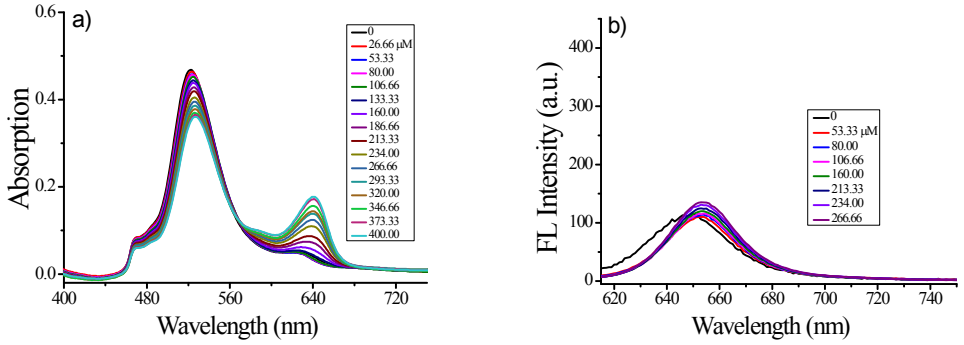


Fig.S17 UV-Vis (a) and fluorescence (b) spectra of probe **SQ** (5 μM) upon addition of TritonX-100 in urine. (λ_{ex} = 600 nm)

S1. Xu, Y.; Li, Z.; Malkovskiy, A.; Sun, S.; Pang, Y. *J. Phys. Chem. B* **2010**, *114*, 8574.